

# On the kinetics of iridium nanoparticles formation in ionic liquids and olefin hydrogenation

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## Abstract

The in situ formation of an iridium nanoparticles dispersion obtained from the reduction of the organometallic precursor  $[\text{Ir}(\text{cod})\text{Cl}]_2$  in 1-*n*-butyl-3-methyl imidazolium hexafluorophosphate ionic liquid by molecular hydrogen is an autocatalytic process. These nanoparticles possess a small size and a monomodal size distribution of  $2.0 \pm 0.4$  nm iridium nanoparticles can be confirmed by TEM and XRD analysis before and after the catalytic process. The 1-decene hydrogenation by the Ir(0) nanoparticles in the ionic liquid follows the classical monomolecular surface reaction mechanism ( $v = \frac{k_c K[\text{S}]}{1 + K[\text{S}]}$ ). The reaction rate is a mass controlled process under hydrogen pressure <4 atm. The catalytic kinetic constant ( $k_c$ ) and the adsorption constant ( $K$ ) under hydrogen pressures  $\geq 4$  atm are independent of the hydrogen concentration indicating zero order dependence on hydrogen pressure and the reaction depends only of the 1-decene concentration in the ionic liquid.

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## 1. Introduction

Without doubt the olefin hydrogenation reactions promoted by transition-metal complexes in homogeneous conditions and by classical heterogeneous catalysts are one of the most investigated catalytic reactions and fundamental aspects such kinetics and mechanism are well known [1,2]. Conversely, little attention has been paid to the kinetics of the hydrogenation reactions catalyzed by soluble transition-metal nanoparticles in one-phase and multiphase conditions [3–8]. The recent advent in metal nanoparticles synthetic control methods has resulted in a new impulse on the synthesis and applications of soluble transition-metal nanoparticles in catalysis, particularly for hydrogenation and C–C coupling reactions [4,9–14]. In this respect, it is expected that soluble transition-metal nanoparticles of 1–10 nm in size will exhibit physical–chemical properties intermediate between those of the smallest element from which they can be composed and those of the bulk material [15,16]. Indeed, in

many cases this new generation of soluble nanoparticles gave singular catalytic activities/selectivities i.e. different from that expected for a molecular (single-site) or heterogeneous catalysts (multi-site) [17,18]. However, in other cases these nanoparticles behaves like classical heterogeneous catalysts [19–28] and in some other cases these soluble materials are decomposed, under the reaction conditions, generating monometallic homogenous catalytic active species [29].

We have recently demonstrated that Ir(0) nanoparticles prepared in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ionic liquid had a small size and monomodal distribution and are stable and active catalysts for the hydrogenation of alkenes and arenes in multiphase conditions [30,31]. We now report the kinetic model for the hydrogenation of olefins by these nanoparticles dispersed in the ionic liquid.

## 2. Results and discussion

The in situ reduction of the organometallic precursor  $[\text{Ir}(\text{cod})\text{Cl}]_2$  (cod = 1,5-cyclooctadiene) dispersed in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF<sub>6</sub>) ionic liquid by molecular hydrogen has been used as catalytic system

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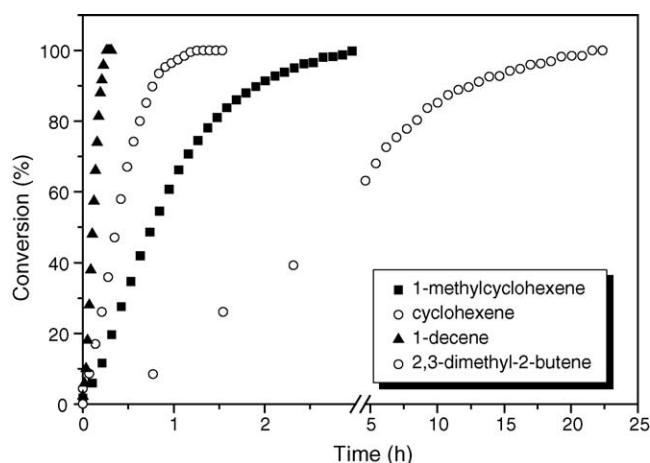


Fig. 1. Hydrogenation of olefins catalyzed by in situ iridium nanoparticles dispersed in BMI-PF<sub>6</sub> (1 mL) at 4 atm constant hydrogen pressure (constant pressure) at 75 °C.

for the hydrogenation reaction of di-, tri- and tetra-substituted olefins and the obtained results are shown in Fig. 1. These results show that there is a strong dependence of the rate of hydrogenation on the structure of the alkene and the observed rate constants decrease in the order 1-decene > cyclohexene > 1-methylcyclohexene > 2,3-dimethyl-2-butene, a reactivity order clearly related with the increase in steric demand of the non-linear substituted alkenes. Similar trend is characteristic of classical homogenous catalysts such as [Ir(cod)(P<sup>i</sup>Pr<sub>3</sub>)(py)]PF<sub>6</sub> [32]. Noteworthy, the isolated and re-dispersed nanoparticles in the ionic liquids gave the same results for the catalytic hydrogenation reactions.

In all cases, hydrogenation by [Ir(cod)Cl]<sub>2</sub> dispersed in BMI-PF<sub>6</sub> (1 mL) ionic liquid has a typical sigmoidal shape with very short induction periods. This kinetic behavior is characteristic of an autocatalytic mechanism and a strong indication of transition metal nanoclusters formation under hydrogen [33]. These experimental curves, as for example for the 1-decene hydrogenation (Fig. 2), can be fitted to the autocatalytic kinetic model that can involve basically: nucleation ( $A \rightarrow B$ ,  $k_1$ ) and autocatalytic surface growth ( $A + B \rightarrow 2B$ ,  $k_2$ ) [33]. The obtained values for the nucleation and autocatalytic growth constants, from the fit of Fig. 2,  $k_1$  and  $k_2$  are 2.04 h<sup>-1</sup> and 5125 M<sup>-1</sup> h<sup>-1</sup>, respectively. Moreover, attempts to fit the curve with a mechanism including a third step, the bimolecular aggregation ( $B + B \rightarrow C$ ,  $k_3$ ) [34,35], or with the recently discovered double autocatalytic mechanism [36,37], which includes a fourth step for the formation of bulk-metal ( $B + C \rightarrow 1.5C$ ,  $k_4$ ), did not converge the fit, which strongly suggests that agglomeration is not significant in this case.

Indeed, TEM analysis (Fig. 3) of the nanoparticles dispersed in BMI-PF<sub>6</sub> before and after catalysis show no sign of agglomeration ( $2.0 \pm 0.4$  nm), indicating that the ionic liquid promote a fundamental stabilization of the nanoparticles at the nucleation step, resulting in particles with a very small size and a monomodal distribution. In addition, XRD analysis shows the presence of broad reflection lines indicating the diffraction by very small crystals. The four diffractions peaks were assigned as

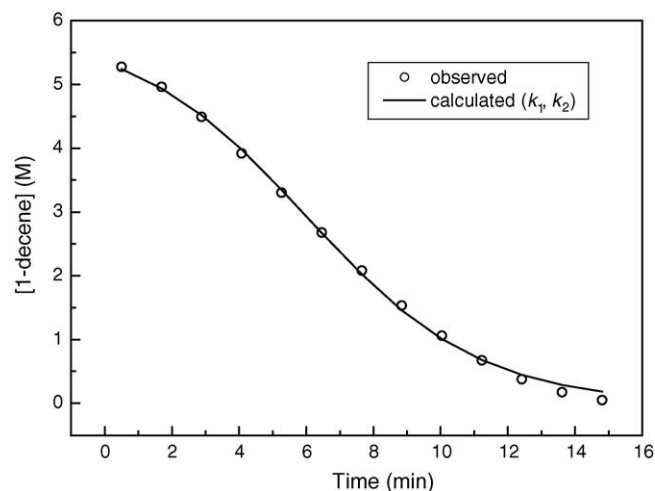


Fig. 2. Hydrogenation curve fits for 1-decene hydrogenation with the catalyst precursor [Ir(cod)Cl]<sub>2</sub> dispersed in BMI-PF<sub>6</sub> (1 mL), 4 atm constant hydrogen pressure at 75 °C. The solid line is the curve fitting using the two steps [ $A \rightarrow B$ ,  $A + B \rightarrow 2B$  ( $k_1$ ,  $k_2$ )] mechanism. The 1-decene/Ir molar ratio is 1215.

correspond to the Ir(0) (1 1 1), (2 0 0), (2 2 0) and (3 1 1) reflection planes. The most representative reflections of Ir(0) were indexed as a face-centered cube (fcc) with unit cell parameter  $a = 3.8784$ . The calculated (using the Scherrer equation) mean diameter of Ir(0) nanoparticles before and after catalysis are 2.1 and 2.3 nm, respectively.

The influence of the substrate/catalyst concentration ratio, hydrogen pressure and reaction temperature has been investigated for the 1-decene hydrogenation. The results obtained with different catalyst precursor concentrations on the 1-decene hydrogenation by the Ir(0) nanoparticles in BMI-PF<sub>6</sub> are presented in Table 1 and Fig. 4. The results show clearly that at a substrate/catalyst ratio of ca. 5000 catalyst saturation occurs, i.e., starting from this “substrate/catalyst concentration ratio”, the frequency turnover (TOF) remains constant. This result suggests that a very important limiting factor of the hydrogenation reaction is the miscibility of 1-decene in the ionic liquid that is around 1.4 mol% at room temperature [38]. Noteworthy that diffusion of reactants is a common rate-determining factor in a variety of reactions and sorption processes performed under multiphase conditions.

Table 1

Influence of the 1-decene/Ir ratio on the catalytic activity for the 1-decene hydrogenation by Ir(0) nanoparticles in BMI-PF<sub>6</sub> (1 mL) at 75 °C and 4 atm of hydrogen (constant pressure)

Entry	Olefin/Ir	Time (h) <sup>a</sup>	TOF (h <sup>-1</sup> ) <sup>b</sup>
1	1215	0.30	4050 (7776)
2	2430	0.33	7363 (14137)
3	4937	0.33	14960 (28723)
4	6583	0.66	9974 (19150)
5	9875	1.33	7425 (14256)
6	19750	1.83	10800 (20736)

<sup>a</sup> Time for 100% of 1-decene conversion.

<sup>b</sup> Turnover frequency mol(1-decene)/mol([Ir(cod)Cl]<sub>2</sub>) h and in parenthesis the corrected turnover frequency (by means of magic-number approach [39]) considering only the exposed atoms on the nanoparticle surface (52%).

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